DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 113

DETERMINATION OF PERMEABILITY OF BALLOON FABRICS

BY

JUNIUS DAVID EDWARDS, Associate Chemist

Bureau of Standards

ISSUED JULY 2, 1918

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By Junius David Edwards

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1. INTRODUCTION

One of the most essential characteristics of a balloon envelope is that it shall be gas tight, or nearly so. Therefore the determination of the permeability of balloon fabrics to hydrogen, which is the gas used in the modern dirigible and kite balloons, is of first importance in determining their suitability for balloon construction. In connection with a study of the permeability of balloon fabrics it has been necessary to investigate different forms of apparatus and the influence of experimental conditions in order to interpret test results intelligently. The results of the

Bureau's investigation of methods of determining permeability are presented in this paper. The effect of composition, method of construction, etc., upon the permeability will not be discussed in the present paper, which deals only with testing methods.

A great many materials have been suggested for rendering fabric gas tight; the great majority of balloon envelopes, however, are made from rubber-coated silk or cotton, usually the latter. For the balloon envelope, two plies of cloth are used with the gas-tight rubber film between them. The two plies may be placed parallel to each other or one ply may be placed at an angle of 45 degrees; the biased fabric is supposed to offer greater resistance to tearing. Usually from 100 to 130 grams of rubber per square meter are placed between the plies. For protecting the fabric and the gas-retaining rubber film from the action of light, heat, moisture, etc., rubber coatings may be applied on the outside; further protection is sometimes added by coating the inside of the fabric also. Lighter single-ply fabrics are sometimes made for use in ballonets and three-ply fabrics find use in large dirigibles or supply balloons.

Goldbeater's skin finds some application in dirigible balloons of the rigid type. Oiled fabrics of various kinds, as well as fabrics coated with lacquers made from cellulose acetate or nitrate, have been tried. Various coatings have also been applied to rubberized fabrics with a view to rendering them more nearly gas tight and increasing their durability. However, none of these has been found entirely successful.

2. THEORY OF PERMEABILITY PROCESS

Gas escapes from a balloon envelope through leaks at valves, seams, and imperfections in the fabric, and by passage through the fabric. Hydrogen might pass through the fabric by diffusion through minute holes in a manner similar to the passage of a gas through a porous plate or it might escape by solution in the rubber film with subsequent evaporation from the other side. As a matter of fact, both processes occur simultaneously. The escape of hydrogen through openings in the fabric is only a case of gas effusion, but the passage of hydrogen through the rubber of the fabric is a very different phenomenon.

Thomas Graham,[1] in 1866, investigated the flow of gases through rubber films and showed that it was a solution phenomenon and

[1] Phil. Mag., 32, p. 401; 1866.

not a diffusion phenomenon. If gases passed through rubber films by diffusion through microscopic holes, their relative rates of escape should be approximately inversely proportional to the square roots of their densities. Graham showed, however, that the rates of penetration of different gases bore no relation to their density. He found the relative rates of penetration of rubber by different gases to be as follows:

Nitrogen	1.0
Methane	2.15
Oxygen	2.56
Hydrogen	5.50
Carbon dioxide	13.58

The rate of change of permeability of rubber films with change of temperature is also much greater than can be accounted for by the diffusion theory. These and other facts have shown that gases penetrate rubber by first dissolving in the rubber.

When a rubber-coated balloon fabric is placed in contact with hydrogen on one side and air on the other, the following process is substantially what occurs. Both the hydrogen and the oxygen and nitrogen of the air dissolve in the rubber film and tend to saturate it up to the limits determined by the temperature and by the partial pressure of each gas. Each gas penetrates the rubber film at its characteristic speed, and when it reaches the opposite side of the rubber film the gas evaporates from its solution in the rubber because the partial pressure of the gas in question is substantially zero. More of each gas is dissolved continuously on the first side of the fabric and a dynamic equilibrium is reached which continues so long as fresh air and fresh hydrogen are available at the two surfaces. In this manner hydrogen passes through the rubber to the air side and air passes through to the hydrogen side.

These facts will be discussed more fully in connection with the experimental work and their bearing on methods of test pointed out.

3. METHODS OF DETERMINING PERMEABILITY

The permeability of a balloon fabric may be defined as the rate at which it is penetrated by a certain gas; except when stated otherwise, this gas is understood in this paper to be hydrogen. Permeability will be expressed in terms of liters of hydrogen per square meter per 24 hours, the volume of hydrogen being cor-

rected to the standard conditions of 0° C and 760 mm mercury pressure.

The methods in use for the determination of the permeability of balloon fabrics to hydrogen may be divided into two classes: (1) Methods which measure the rate of decrease in volume of a mass of hydrogen separated from the atmosphere by a definite area of the fabric; or (2) methods which measure by chemical or physical means the volume of hydrogen passing through a definite area of fabric in a given period.

The two methods may be characterized as the volume loss and penetration methods, respectively. According to the definition of permeability just given the volume-loss method does not measure the permeability of a fabric because in the volume-loss method the quantity measured is the volume of hydrogen escaping minus the volume of air passing into the hydrogen chamber.

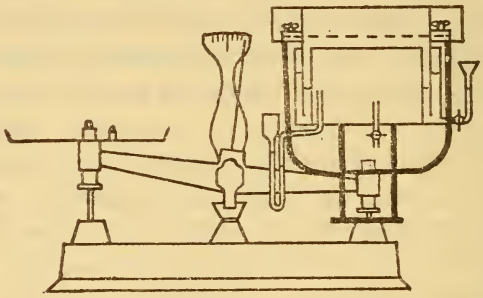

FIG. 1.—*Renard-Surcouf balance*

What it measures is the difference in the permeability of the fabric to hydrogen and air. Accordingly, any result obtained with this method will be characterized as the "volume-loss" permeability.

(*a*) *Volume-Loss Methods.*—The most widely used apparatus for applying the volume-loss method is known as the Renard-Surcouf balance. As shown in Fig. 1, it consists of the bell of a small gas holder mounted on one arm of a balance; the top of the bell is closed by the fabric (shown by a dotted line) under test. The bell moves up and down in an annular space filled with water; the annular container is attached to the base of the balance. The bell is first filled with hydrogen by alternately filling and emptying until the air has been displaced. The proper pressure is then obtained by adding weights to the opposite balance arm. As hydrogen escapes, the bell sinks, and the pointer moves over a calibrated scale indicating the volume loss. The apparatus should be kept in a constant temperature chamber.

Five other forms of apparatus of this class are described by Austerweil.[2] In each of these forms of apparatus a gas chamber filled with hydrogen is closed by the fabric under test. A graduated measuring tube is connected with this chamber and the volume of hydrogen escaping is measured by the volume of water necessary to replace it and maintain constant pressure. A leveling bottle may be used to introduce water into the measuring tube or it may be connected with a Mariotte flask which automatically introduces the water under constant pressure. If a leveling bottle is used, the pressure does not remain constant and must be adjusted at frequent intervals. The operating characteristics of this class of apparatus are discussed in section 6.

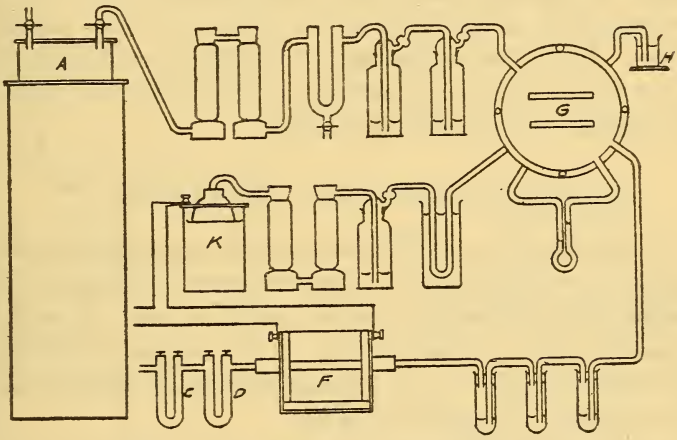

FIG. 2.—*Apparatus of Barr and Rosenhain*

(*b*) *Penetration Methods.*—The various forms of apparatus for applying the penetration method all employ a cell which is divided by the fabric into two chambers. In one of these chambers an atmosphere of hydrogen is maintained at a definite pressure. Through the other chamber is passed a stream of air which carries away the hydrogen as it penetrates the fabric. The amount of this hydrogen is determined by burning it to form water and weighing the water after absorption in some suitable medium, or the percentage of hydrogen is determined in the stream of air passing over the fabric by means of the gas interferometer.

The apparatus of Barr and Rosenhain,[3] as used in the National Physical Laboratory, is shown in Fig. 2. The hydrogen from the

[2] G. Austerweil, Die Angewandte Chemie in der Luftfahrt. Published by R. Oldenbourg, München, 1914.

[3] Report of the British Advisory Committee for Aeronautics, p. 86, 1909–10.

electrolytic cell *K* passes through a series of washing and drying tubes into the permeability cell *G* and out through the water seal *H*. The air from the gas holder *A* after passing through a series of washing and drying tubes passes over the other side of the fabric, then through another series of drying tubes, through an electric furnace *F*, where the hydrogen is burned, and finally through the absorption tubes *C* and *D* which are to be weighed. The permeability cell is kept in a constant temperature bath.

The apparatus described by Heyn[4] and used at the Physikalischen Reichsanstalt is similar in principle though differing in form and detail.

Frenzel[5] made a notable improvement in this method by employing a Rayleigh-Zeiss gas interferometer for determining the concentration of hydrogen in the air stream after passing over the fabric. From the percentage of hydrogen so determined and the rate at which the air was passing, as determined by a gas meter, the permeability was easily calculated.

4. EXPERIMENTAL APPARATUS

In the investigation of different testing methods several forms of apparatus were employed. The most useful apparatus and the one employed in all routine testing work as well as most of the experimental work is shown in Fig. 3. It applies the penetration method and employs a gas interferometer for determining the hydrogen passing through the fabric.

In this apparatus, the fabric is held in the premeability cell *a*, maintained at constant temperature in an air or water bath *h*. Pure, dry hydrogen passes over one side of the fabric and out through a water seal *g*.

Air after passing through the wet-pressure regulator *c* and a length of capillary tubing to reduce pressure fluctuations, is dried by bubbling through concentrated sulphuric acid in *e* and then passed over the other side of the fabric through a drying tube d^1 and into one chamber of the interferometer. It passes out through the drying tube d^2, which prevents diffusion of water vapor into the interferometer and then through the saturator *f* filled with glass beads partly covered with water and then through the wet meter *m*. The saturator is employed to prevent loss of water from the meter by evaporation into the gas being measured.

[4] Sitz. der König. Akad. Wiss., p. 365, 1911.

[5] "Uber die Gasdurchlässigkeit der Gummierten Ballonstoffe." Zs. fur Flugtechnik und Motorluftschiffahrt, 5, p. 264, 1914.

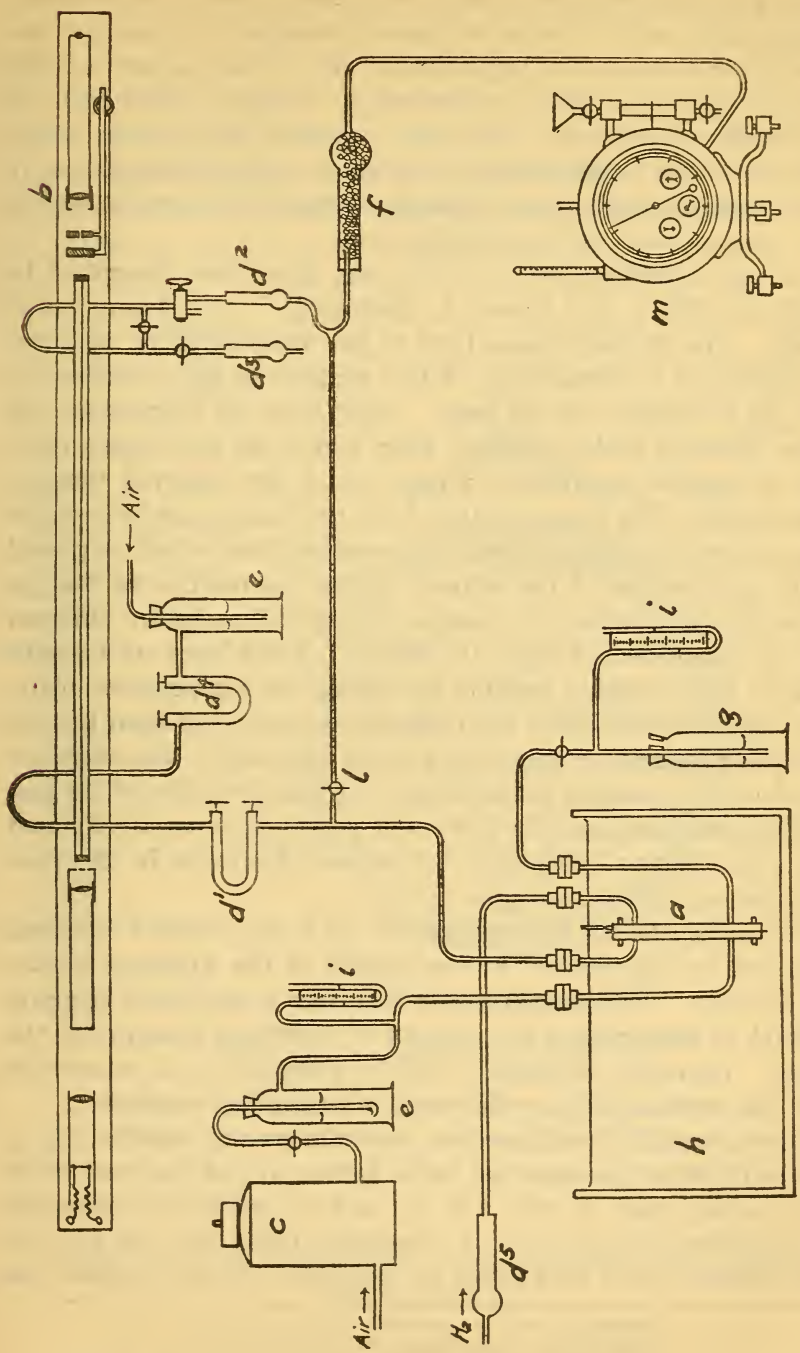

FIG. 3.—*Diagram of Bureau of Standards apparatus*

When the interferometer is being read, the air stream is by-passed through the cock *l* into the wet meter so as not to interrupt the flow of air through the permeability cell. The pressure on the air and hydrogen sides is measured by U-gages *i* filled with oil and water, respectively. Dry air is passed through the other chamber of the interferometer to serve as a comparison gas, or it may be passed through both chambers when it is desired to obtain the "zero reading" of the interferometer.

The gas interferometer and its uses have been described in detail by Haber and Lowe,[6] L. Stuckert,[7] L. H. Adams,[8] and others. The Rayleigh-Zeiss type of gas interferometer measures the difference in refractivity of two samples of gas contained in two gas chambers 100 cm long. Light from an illuminated slit passes through both chambers, after which the two beams combine to produce interference fringes which are observed through an eyepiece. The optical paths of the two beams can be brought to equality by tilting a glass compensator plate which is placed in the path of one of the beams. If the composition of the gas in one of the chambers is changed, the optical paths are different and the interference fringes are shifted. The fringes are brought back to their original position by tilting the compensator plate. The angle through which the compensator plate has been turned, which is measured by means of a drum attached to the micrometer screw, is a measure of the change in refractive index of the gas.

The instrument used for this work was of such sensitivity that one scale division indicated 0.01 per cent hydrogen in air when using air as a comparison gas.

The calibration of this instrument by a new method has been discussed by the author[9] in the Journal of the American Chemical Society. The interferometer furnishes a rapid and accurate method of determining the amount of hydrogen penetrating the fabric. Its many advantages will be pointed out in connection with the various subjects discussed in succeeding sections.

The permeability cells used are shown in greater detail in Fig. 4. The cell adopted as standard had a fabric area of 250 cm^2; other cells having areas of 1000, 100, 50, and 25 cm^2 were constructed for experimental purposes. In designing these cells the gas and air chambers were kept small in volume in order to reduce the

[6] Haber and Lowe, Zs. f. Angew. Chem., 23, p. 1393: 1910.
[7] Stuckert, Zs. f. Elektrochemie, 16, p. 37: 1910.
[8] L. H. Adams, J. Am. Chem. Soc., 37, p. 1181: 1915.
[9] Edwards, J. Am. Chem. Soc., 39, p. 2382: 1917.

space which must be swept out when operating. A large mesh-wire screen (3 cm openings) kept the fabric from being pressed against the back of the air chamber by the pressure of the hydrogen. The flanges of the cell contain a number of very fine grooves which take up the excess of grease used to make the fabric gas tight; they also give a better grip on the fabric. The two halves of the cell are held together by bolts and wing nuts (not shown in figure).

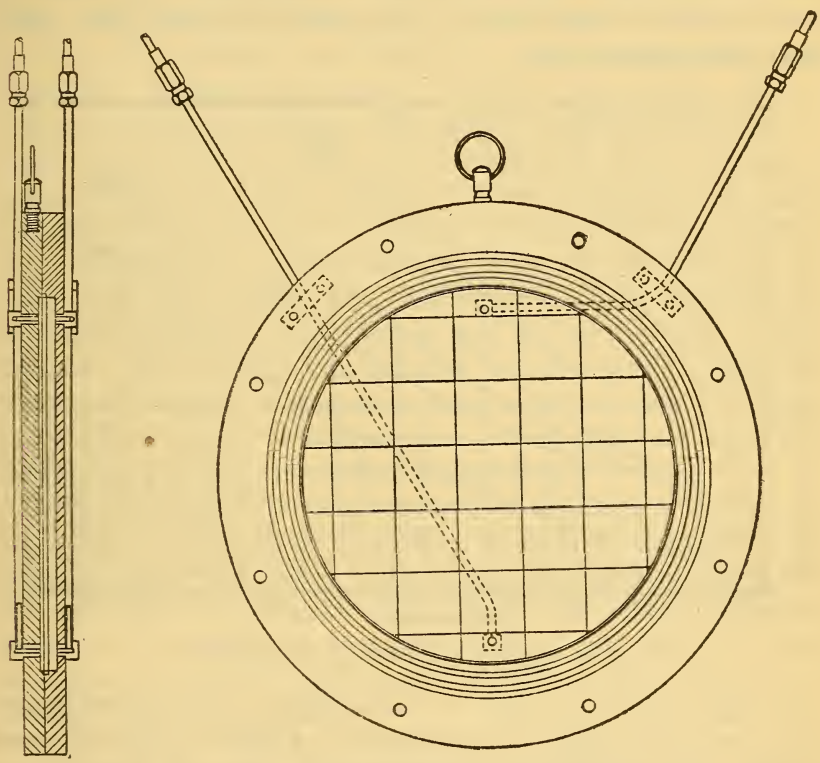

FIG. 4.—*Bureau of Standards permeability cell*

Connections to the gas and air lines and interferometer were made with small metal unions, and copper and glass tubing was used in making the connections to the various parts of the apparatus where necessary.

5. EFFECT OF EXPERIMENTAL CONDITIONS ON APPARENT PERMEABILITY

In order to interpret tests made under different conditions and and with different apparatus, the effect of experimental conditions on the apparent permeability was investigated. The appa-

ratus shown in Fig. 3, with various modifications, was used for all the work reported in this section. The general conclusions reached are applicable to all apparatus of this type whether the hydrogen is determined by combustion or by use of an interferometer; the operating details of the apparatus, however, may be quite different. The interferometer was used in preference to the combustion method because it greatly facilitated the testing work in point of speed and accuracy and permitted the carrying out of certain experiments which would otherwise have been impossible of execution.

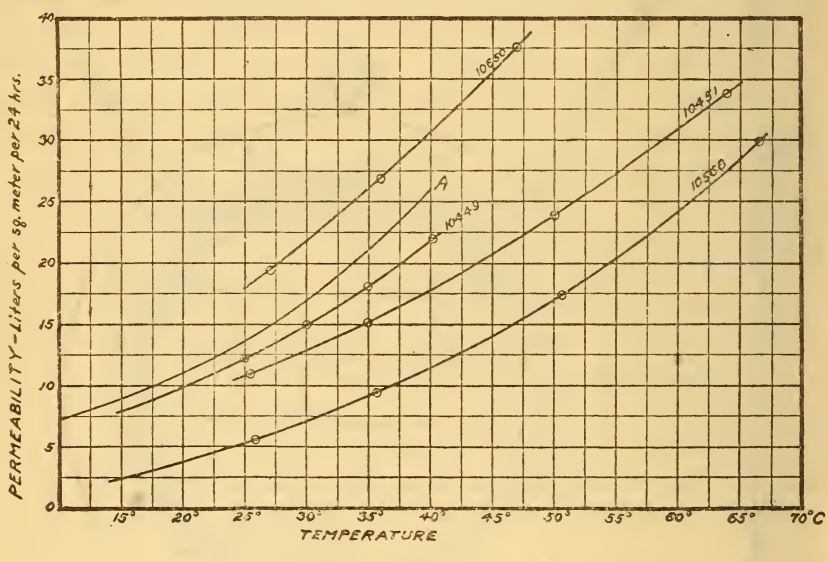

FIG. 5.—*Effect of temperature on permeability*

(*a*) *Effect of Temperature on Permeability.*—It has been known for a long time that the permeability of rubber films increases rapidly with increase of temperature.[10] For this reason it is necessary in all accurate work to maintain the fabric at a constant temperature during the period of test.

The rate of change of permeability with change of temperature for a number of different fabrics is shown in Fig. 5. In determining these curves the cell containing the fabric was mounted in an air bath, which was maintained at the desired temperature by means of an electric heater controlled by a thermostat. The fabric was allowed to come to equilibrium and its permeability determined at each temperature before changing

[10] Graham, Phil. Mag., 32, p. 401; 1866.

to the next temperature. Curves 10449, 10451, and 10650 show the temperature coefficients of fabrics from three American manufacturers and curve 10568 is for a fabric of foreign manufacture. These curves are all very similar in shape, indicating that, approximately at least, the same relation between permeability and temperature holds for fabrics of quite different composition. For purposes of comparison, another curve showing the change of permeability with temperature as determined by other experimenters is included. This curve *A* is taken from the report of Gibbons and Smith;[11] it shows substantial agreement with the Bureau's results. Frenzel[12] gives graphs for four continental balloon fabrics. They show a smaller rate of change than any of the preceding curves and indicate the change of permeability to be a linear function. None of the fabrics examined by this Bureau have shown a linear relation between temperature and permeability. Communications from private testing laboratories here and abroad show temperature effects corresponding to those obtained at the Bureau and do not indicate a linear relation. Two tests at two different temperatures by Rosenhain and Barr[13] indicate a somewhat more rapid increase of permeability with increase of temperature. Their data are insufficient to warrant any general conclusions, however.

In order to make the tests comparable, the Bureau of Standards has adopted the practice of making all tests at a standard temperature of 25° C. This temperature was adopted because of the ease and convenience with which the testing apparatus could be maintained at this temperature, and because it was thought to represent with some degree of approximation an average balloon temperature.

The National Physical Laboratory, England, has adopted 15.5° C (60° F) as its standard temperature. That temperature can not be maintained in most American testing laboratories in summer without refrigeration, which needlessly complicates the testing. The customary practice in France is to use 15° C as the standard temperature. However, temperature control of the Renard-Surcouf balance, which is the most widely used instrument there, is rather difficult, and it is not known what degree of uniformity there is in temperature control in French practice.

[11] First Annual Report of the National Advisory Committee for Aeronautics (Washington, 1915), p. 171.

[12] Frenzel, "Über die Gasdurchlässigkeit der Ballonstoffe." Drückerei des Elsässichen Textilblattes im Gebweiler.

[13] Report, Great Britain Committee on Aeronautics, p. 60; 1910–11.

For the purpose of approximate comparisons, the permeability of the average rubberized fabric at 15° C may be taken as 65 per cent of the permeability at 25° C.

(*b*) *Effect of Pressure on Permeability.*—It has been customary, both here and abroad, to determine the permeability of balloon

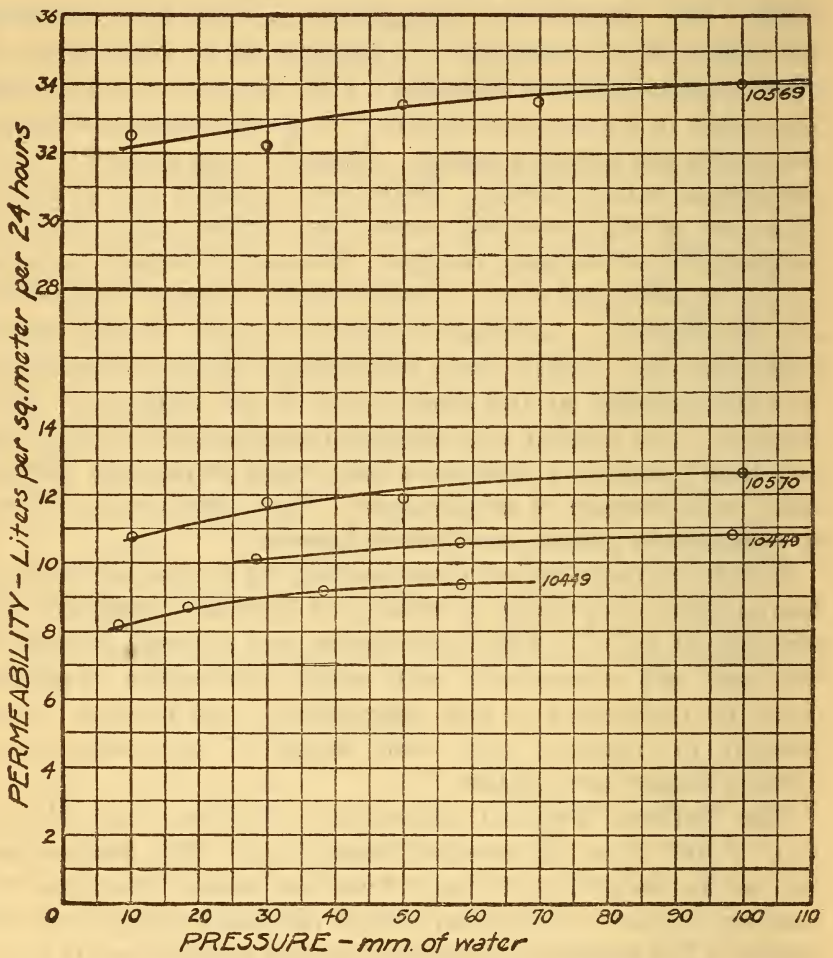

FIG. 6.—*Effect of pressure on permeability*

fabrics under a pressure of hydrogen equivalent to 30 mm of water. This is approximately the normal working pressure of a nonrigid balloon.

The pressure coefficient for two-ply balloon fabrics has been found to be rather small. The rate of change of permeability with change of hydrogen pressure for three fabrics is shown in Fig. 6.

The change in permeability with change in pressure is very small, above 50 or 60 mm the curve being almost horizontal. The greater effect of pressure change at low pressures may be due, as suggested by Frenzel, to the fact that the initial increases of pressure stretch both the rubber film and the supporting fabric, but the point is soon reached where further stretch of the rubber film is prevented by the relatively inelastic fabric, and thereafter the permeability shows only a very small change. The effect of pressure as well as of temperature varies somewhat with different fabrics, but with those tested it was small. This is to be expected, since an increase of hydrogen pressure of 10 mm of water (0.74 mm of mercury) means an increase of only about 0.1 per cent in the total pressure of the hydrogen.

Since the permeability is approximately proportional to the partial pressure of hydrogen (see p. 22), the permeability should vary with the atmospheric pressure, because the partial pressure of the hydrogen is equal to the atmospheric pressure plus the constant excess pressure under which it is confined in the cell. However, the changes in barometric pressure are usually small, seldom more than 1.5 per cent; accordingly, they have been neglected in routine testing since their effect upon permeability, as far as can be ascertained from an examination of test results, is within the limits of experimental error. It should be noted that it is the excess gas pressure above atmospheric which produces the greatest part of the increase noted at the beginning of the curves shown in Fig. 6.

(*c*) *Effect of Humidity of Hydrogen and Air.*—The influence of moisture upon the permeability was determined by comparing the permeability shown when using dry hydrogen and air with the permeability when using moist hydrogen and air. When dry gas was to be used, it was passed through concentrated sulphuric acid; when moist gas was employed, it was passed through sulphuric acid of such concentration that the relative humidity of the saturated gas was approximately 65 per cent at 25° C.

The permeability of a fabric was determined with dry gas and then with moist gas; the order was then reversed. The same difference was noted in each case when testing under the two different conditions. The average results of these tests are given in Table 1.

TABLE 1.—Effect of Humidity of Hydrogen and Air on Permeability

Order of test	Condition of hydrogen and air	Permeability, liters per square meter per 24 hours	Difference	Order of test	Condition of hydrogen and air	Permeability, liters per square meter per 24 hours	Difference
First test	Wet	13.8		First test	Wet	13.7	
Second test	Dry	14.4	0.6	Second test	Dry	14.5	0.8
First test	do	15.1		First test	do	14.6	
Second test	Wet	14.5	.6	Second test	Wet	13.9	.7

When the hydrogen is 65 per cent saturated at 25° C there is approximately a 2 per cent decrease in the partial pressure of the hydrogen due to the addition of water vapor. This partially explains why a 4 to 5 per cent decrease in permeability was noted when changing from dry gas to wet gas. The amount of water dissolved in the rubber probably also influences the rate of penetration of the rubber by the hydrogen.

Tests showed that the moisture contained in the fabric was not completely removed by a current of dry air at 25° C after a number of hours' passage, so that it is certain that the rubber compounds under the conditions of test with dry gas still contain an appreciable amount of water vapor.

No further experiments on the effect of moisture were made, since it was evident that the difference in permeability under the two conditions of test was small—less than 1 liter in this case. For testing purposes the conditions of test which are recommended should be easily obtained and duplicated, and it is obvious that the use of dry hydrogen and air is most satisfactory in every respect. It does not introduce further complications in calculations and testing, and gives results very close to those obtained with partially saturated gas.

(*d*) *Effect of Volatile Substances in Fabric.*—The apparent permeability may be affected by the removal of volatile substances from the fabric by the current of air passing over it. There may be present in the air stream after passing over the fabric varying amounts of water vapor, carbon dioxide, or the vapor of benzol, gasoline, or other solvent used in the manufacture, in addition to the hydrogen which has penetrated the fabric. The water vapor and carbon dioxide which may have been dissolved in the rubber are removed by soda lime and calcium chloride before the air

stream enters the interferometer. In case the combustion method is used, only the water vapor need be absorbed.

The presence of vapor of solvents, however, introduces a possible serious source of error into either method. If the hydrogen is estimated by use of the interferometer, the apparent permeability is too low, because the refractivity of solvent naphtha or benzol is higher than the refractivity of air or hydrogen. If the combustion method is used, the results are too high by the amount of water formed by the combustion of the solvent. This point should be carefully considered when testing fabrics of very recent manufacture, and it is of great importance in the commercial control of fabric manufacture. It is usually assumed that the solvent used in the rubber coatings when they are spread is entirely removed by the subsequent heating and curing. In some cases, notably three-ply fabrics with heavy rubber coatings, sufficient solvent may be left to seriously vitiate test results unless it is removed or corrected for. Its presence can sometimes be detected from the odor of the fabric.

The necessary correction for solvent vapor can be readily found by determining the reading of the interferometer when using air in place of hydrogen in the permeability cell. Since the amount of solvent given off by the fabric decreases with time, it is necessary to take at least three readings at short intervals to determine the rate of change of the blank; the correction at the time of the permeability test, which should follow immediately, is estimated by extrapolation. This method does not necessitate waiting for the complete removal of the solvent before beginning the test, and for most purposes is sufficiently accurate. It is of course obvious that a more accurate method would be to wait until the solvent is completely removed, thus eliminating the necessity for a blank correction.

The estimation of the blank correction is more difficult in case the combustion method is used, because it is impracticable to determine its rate of change. Its magnitude may be determined, however, and if a more accurate determination is required, a number of permeability tests can be made at suitable intervals.

Of several hundred samples tested at the Bureau only fabrics of a certain composition have shown blanks of appreciable magnitude. The possibility should not be overlooked, however, in the case of any fabric with heavy rubber coating and of very recent

manufacture, particularly if the presence of solvent can be detected by the odor.

(*e*) *Duration of Test.*—The passage of hydrogen through the fabric being a solubility phenomenon, it may be assumed that a certain time must elapse after the fabric is placed in contact with hydrogen before the fabric is saturated with hydrogen and reaches its maximum permeability. The interferometer lends itself readily to the investigation of this point, since readings may be taken at short intervals.

Care should be taken not to confuse the time required for the air-hydrogen mixture to reach equilibrium throughout the apparatus with the time required for the fabric to reach equilibrium. The larger the air chamber in the cell and the greater the volume of the rest of the air system, the longer is the time required for the hydrogen given off from the fabric to reach a uniform concentration throughout the apparatus. It was with this point in mind that the cells were designed with as small gas chambers as seemed practicable.

The results of 200 representative determinations were examined to ascertain what effect the duration of the test had upon the apparent permeability. In making these determinations, which were mainly of a routine nature, the first reading was usually taken 30 minutes after starting the test. Three or four readings at intervals of approximately 30 minutes were taken in order to determine whether a constant value was being reached. These results, together with the experience obtained in some 500 other tests, show that the time required for the fabric to reach its maximum permeability is almost always less than 1 hour and usually less than 30 minutes.

Other workers have stated that periods of from 3 to 5 hours were necessary before the fabric reached its maximum permeability. Where experiment seemed to indicate this, the time was probably required for the air stream itself to reach equilibrium and not the fabric. For any apparatus the preliminary sweeping-out period should be experimentally determined.

It has been noted that in continued testing of the same piece from day to day there was usually a gradual decrease in the permeability. For example, a certain test piece (No. 52), which had an initial permeability of 15.1 liters, showed on the 3 succeeding days permeabilities of 14.8, 14.6, and 14.4 liters. Sometimes the decrease was more rapid; another fabric (test No. 518), showed a

decrease from 21.4 to 19.2 liters in 5 successive half-hour tests. One very unusual 3-ply fabric with extra heavy rubber coatings consistently showed a large decrease; 1 test piece, for example, changed in permeability from 18.9 to 14.5 liters in 8 successive tests on the same day. The same test piece changed from 16.4 to 11.3 liters on the following day. Four months later another test piece from the same sample indicated in 5 successive half-hour tests permeabilities of 17.2, 16.1, 14, 13.6, and 12 liters. However, the great majority of fabrics tested give quite consistent and constant results during the period of test. Using the combustion method, where a considerable period of time is necessary for each test and usually only one observation is made, the changes noted above would usually pass unobserved.

A similar decrease in permeability is obtained by heating the fabric. Test piece No. 52, previously referred to, showed a permeability of 14.4 liters at the last test. Without removing it from the cell or interrupting the test its temperature was raised to 70° C and held at that temperature for 30 minutes. On lowering the temperature to 25° again its permeability was found to be 10.8 liters, and on the 3 succeeding days it was 10.9, 10.9, and 11 liters. Another test piece showing an initial permeability of 11.7 liters was heated to 50°, held at that temperature for 30 minutes, and then allowed to cool again, the whole process requiring about 3 hours. Its permeability was found to have decreased to 8.5 liters. Fabric heated in an electric oven before testing and before coming in contact with hydrogen showed a similar decrease in permeability, the magnitude of the effect depending upon the temperature and time of heating. Samples exposed to the weather also gradually acquire a lower permeability. This, however, is accompanied by a hardening process, which eventually leaves the rubber film so brittle as to be useless.

This variation in the permeability of a rubber film under the conditions noted makes it impossible to use one test piece in a long series of experiments and yet secure comparable results. New pieces must be used to secure comparable samples, and they are subject to any variation due to nonuniformity of the material.

In conclusion, it may be said that the permeability of most samples remains practically constant during a day's test. Longer testing will probably show a decrease. Occasionally a fabric will be met with that shows a very large decrease during the test. Heating a fabric will produce a very appreciable decrease in per-

meability. An explanation of the changes occurring in the rubber which cause the changes in permeability noted will not be given at this time.

(*f*) *Rate of Air Flow.*—Tests made over an extended period with different fabrics and different permeability cells showed that, within wide limits, changing the rate of passage of air through the cell did not make any significant change in the apparent permeability. The air rate in both large (250 cm^2) and small (100 cm^2) cells was varied from 1 to 3 liters per hour; the normal rates were 1.5 and 2.5 liters per hour. The tendency toward slightly higher results when the rate was increased was occasionally noted, but the effect was not consistently observed; usually any change was well within the accidental variations in the results. It may be concluded, therefore, that within working limits, differences in the air rate are unimportant as affecting the result. It should be noted, however, that a uniform air rate must be maintained during the test in order to secure satisfactory results. This is especially important where the interferometer is being used, since it is assumed that the concentration at the time of observation is the same as during the preceding period when the rate was being determined by the meter; this would only be true in case the permeability and rate of air flow remained constant

(*g*) *Effect of Size and Shape of Cell on Apparent Permeability.*—The size and form of the cell might have an effect on the apparent permeability of a fabric being tested in it if the cell did not permit uniform circulation of the hydrogen and air currents over the entire area of the test piece. If the air is not readily swept out of the hydrogen chamber or if the hydrogen passing through the fabric is not uniformly removed by the air stream, the results with different cells might vary. The significant factors of cell design have been examined to determine what effect they have upon the apparent permeability.

The first point considered in the design of the cell was the size of the test piece and the form of the hydrogen and air chambers. The method depends of course upon reaching an equilibrium condition throughout the system with practically pure hydrogen on one side of the fabric and a uniform distribution throughout the interferometer system of the hydrogen passing through the fabric. Therefore, the smaller the volume of the gas chambers in the cell, the sooner will this equilibrium condition be reached, providing, of course, that the fabric is being penetrated by hydrogen at its

maximum rate under the given conditions. On the other hand, the area of the test piece must be large enough to give sufficient concentration of hydrogen at a suitable air rate for the required accuracy in the interferometer reading.

For most work a test piece having an area of 250 cm^2 is satisfactory. The construction of the cell adopted as standard is shown in Fig. 4. The hydrogen chamber has a depth of 2 mm; the pressure of hydrogen (30 mm of water) is sufficient to keep the fabric from coming in contact with the cell wall. The air chamber is 4 mm deep; to prevent the pressure of the hydrogen from forcing the fabric against the opposite side of the chamber a large-mesh wire screen is placed in the cell. Three cells of this type and a fourth exactly similar, except that the air chamber is 6 mm deep, are in constant use. Intercomparison shows that all four give practically identical results with the same fabric. Equilibrium is reached very quickly with a cell of this type. (See p. 18.)

A smaller cell having an area of 100 cm^2 and a hydrogen chamber 20 mm deep was modified by filling up the hydrogen chamber with paraffin until the gas space was only 2 to 3 mm deep. With the original hydrogen chamber of 20 mm depth the fabric did not reach its maximum permeability until several hours after starting the test, even though the rate of passage of the hydrogen was several times the normal rate. With the hydrogen space restricted a constant permeability was reached 30 minutes after starting the test.

The cells are normally used in a vertical position. To determine whether this had any effect on the result, a cell was operated in various other positions. As was to be expected, no effect due to position was observed.

In a similar manner the effect of direction of gas flow was tested. With a cell suspended in a vertical position it made no difference in the apparent permeability whether the air was introduced at the top or at the bottom of the cell. In operation it is our practice to introduce the hydrogen into the cell at the top and the air at the bottom, on the theory that the cell will be swept out more rapidly. It probably makes little, if any, difference, however, if the chambers are small and the gas current sufficiently rapid.

To determine what effect the area of the test piece had on the apparent permeability, cells of different sizes were constructed. These cells had fabric areas of 50, 100, 250, and 1000 cm^2.

If the hydrogen which passes through the fabric is not rapidly removed from the surface, the partial pressure of the hydrogen might become sufficiently great to lower the apparent permeability appreciably. Any such increase of the partial pressure of hydrogen at the surface of the fabric is prevented by the high rate of diffusion of hydrogen. The accumulation of hydrogen in the cell is prevented by the current of air which reduces the average concentration of hydrogen in the cell to 1 per cent or less. For these reasons it is to be expected that the apparent permeability would be independent of the rate of air flow and of the area of exposed fabric within rather wide limits.

The results of a series of tests with these cells showed that these conclusions were substantially correct. The small (50 cm^2) cell gave practically the same apparent permeability as the 250 cm^2 cells but the results were less concordant. The agreement between the 100 and 250 cm^2 cells was very good. With the 1000 cm^2 cell apparently a longer time was required to reach equilibrium.

If the hydrogen is able to penetrate laterally between the plies (see footnote 15, p. 25) the effective area of exposed fabric may not be defined by the edge of the gas chamber but may be somewhat larger. This edge effect would of course be proportionally greater in a small cell than in a large one. However, no such consistent difference was noted.

(*h*) *Concentration of Hydrogen.*—The tests discussed so far were made with hydrogen of approximately 100 per cent purity. If the concentration of the hydrogen in contact with the fabric be reduced by admixture of air, it seems probable that the apparent permeability of the fabric to hydrogen will be reduced about proportionally. Barr and Thomas [14] conclude from two experiments with mixtures of air and hydrogen that the permeability is directly proportional to the partial pressure of the hydrogen.

No tests of this point have been made as yet at the Bureau, since for testing purposes the use of pure hydrogen is desirable from every standpoint and it is known that if the hydrogen contains air, the apparent permeability to hydrogen will be reduced about proportionally. This is an important point to consider in connection with volume-loss methods, since the diffusion of air into the hydrogen chamber will lower the partial pressure of the hydrogen and consequently the apparent permeability.

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[14] Report Great Britain Committee on Aeronautics, 4, p. 270: 1912.

6. VOLUME-LOSS METHOD

Because of the comparative simplicity of the volume-loss method it is important to determine the precision and reliability of results obtained with that method. In the discussion of the theory of the permeability process it was stated that the penetration of the fabric by the hydrogen was accompanied by a simultaneous passage of air through the fabric in the opposite direction. For this reason the volume loss determined is not the hydrogen which has escaped but that volume less the volume of air passing through the fabric into the hydrogen chamber. It is of interest to know what the numerical relation between results determined by the two methods is; also, if there is any great variation in the relative rates of penetration of rubber films by hydrogen and air, it is a fact of importance.

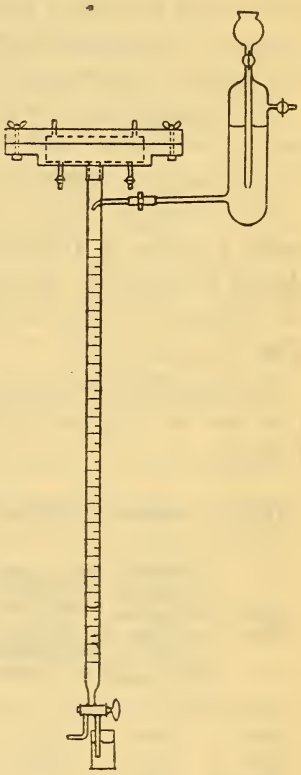

FIG. 7.—*Volume loss apparatus*

(*a*) *Apparatus.*—For investigating the volume-loss method, the apparatus shown in Fig. 7 was designed. It consists of a cell similar to that shown in Fig. 4 and identical with the cell of that type having an area of 100 cm^2 except that the hydrogen chamber is considerably larger (volume = 275 cm^3).

The large volume of the hydrogen chamber prevents any considerable reduction of the partial pressure of the hydrogen through the small volumes of air which diffuse inward. Attached to the hydrogen chamber is a graduated measuring tube which is connected by the orifice shown near the top with a constant-pressure flask. As hydrogen escapes through the fabric, water from the constant-pressure flask drops into the burette through the orifice to take its place. The decrease in volume of the confined gas is determined by the increase of volume of water in the burette. The total volume of the gas space is known and corrections are applied for the changes in temperature and pressure which may occur during the test. Since the fabric

changes temperature with the surroundings, a further correction is necessary for the change of permeability of the fabric with change of temperature.

In operation, the fabric was clamped tightly between the well-greased flanges of the cell. The gas chamber was then tested for leaks by placing it under a small pressure of air. If it was air-tight, the air in the gas chamber and burette were swept out with hydrogen, and the chamber left filled with hydrogen under a pressure of 30 mm of water. The decrease in gas volume was then noted at 30-minute intervals. A current of air was passed through the upper chamber during the period of test.

This apparatus is similar in principle to the apparatus of Lebaudy, Sabbatier, and others and combines their best features. It was developed primarily for experimental purposes.

(*b*) *Results of Tests.*—The results obtained with this apparatus, using a series of fabrics from three different manufacturers, are shown in Table 2. For purposes of comparison the permeabilities of the same fabrics as determined with the apparatus shown in Fig. 3 are included.

The conclusions drawn from these results and the experience in the use of this and similar apparatus may be summarized as follows:

TABLE 2.—Apparent Permeability as Determined by the Volume-Loss Method

Fabric No.	Apparent permeability at 25° C by volume-loss method, liters per square meter per 24 hours	Permeability at 25° C by penetration method, liters per square meter per 24 hours	Ratio of permeabilities	Fabric No.	Apparent permeability at 25° C by volume-loss method, liters per square meter per 24 hours	Permeability at 25° C by penetration method, liters per square meter per 24 hours	Ratio of permeabilities
22152	10.9	15.8	0.69	10652	14.4	20.1	0.72
22151	11.0	15.8	.70	22795	9.8	14.4	.68
22150	12.0	17.9	.67	22496	9.9	15.0	.66
10449	10.7	14.5	.74				
10650	12.4	17.1	.72				Av. .69
10651	7.2	11.0	.65				

With this size of cell the actual volume of hydrogen escaping per hour is usually small and the errors of measurement relatively large. The results are not very concordant and the precision secured is low compared with the standard apparatus.

Great care must be taken to secure a gas-tight joint between the fabric and the cell in order to prevent any leakage other than

through the fabric. A small leak in the hydrogen chamber of apparatus of the penetration type is unimportant, but with the volume-loss method it is fatal to accuracy. Even if this joint is gas-tight, hydrogen may escape from the cell by leaking out between the plies of the fabric. Excessive permeabilities indicated in several cases were traced to this source.[15] To guard against this, if possible, the edges of the fabric were coated with shellac. Where a high permeability is indicated, the results are usually open to the suspicion of being influenced by a leak.

(*c*) *Relation of Volume-Loss to Penetration Method.*—To determine the theoretical relation between the volume-loss and penetration methods it is necessary to know the relative permeability of balloon fabrics to air and to hydrogen.

According to the figures given by Graham (p. 5) the relative rates of penetration of rubber by nitrogen, oxygen, and hydrogen are 1, 2.56, and 5.5. Since the permeability is proportional to the partial pressure, the relative permeability to hydrogen and air would be as $\frac{5.5}{(0.79 \times 1 + 0.21 \times 2.56)}$, which is as 4.1 is to 1. These figures, of course, will vary with different rubber compounds and different experimental conditions.

The rates at which hydrogen and air penetrate a balloon fabric have been determined simultaneously by using two interferometers. With the standard cell (Fig. 4) the hydrogen passing into the air stream was determined in the usual manner. The air passing into the hydrogen in the other chamber of the cell was determined at the same time in another interferometer by comparison with hydrogen from the same source which had not passed through the cell. The calibration of the interferometer was somewhat in doubt in this latter case owing to the fact that the "air" in the hydrogen may have a different ratio of oxygen to nitrogen[16] than in atmospheric air (see p. 5), but if the oxygen content was as high as 40 per cent, the readings would be approximately only 3 per cent low. This difference falls within the rather large experimental uncertainty in these tests; accordingly no correction has been made. This was allowable since the ratio to be determined is not a constant and the results are sufficiently concordant for present purposes.

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[15] Fabric No. 10653 consistently permitted gas to leak between the plies of the fabric and out at the edge of the test piece.

[16] "Air" after passing through a rubber film usually contains more than 21 per cent oxygen because of the higher permeability of rubber to oxygen than to nitrogen.

TABLE 3.—The Permeability of Balloon Fabrics to Hydrogen and Air

Fabric No.	Permeability to hydrogen, liters per square meter per 24 hours	Permeability to air, liters per square meter per 24 hours	Ratio hydrogen to air rate
10652	29.5	8.4	3.5
26995	17.6	4.4	4.0
26293	14.2	3.8	3.7
24753	5.4	1.4	3.9
			Av. 3.8

Table 3 shows the results for four different fabrics. The average ratio of hydrogen to air is about 3.8 to 1. This ratio seems to be approximately constant for rubber-coated balloon fabrics of the type now in use. This would indicate that the volume-loss method should give results which are approximately 74 per cent $\left(\frac{2.8}{3.8}\right)$ of the penetration method, since while 3.8 liters of hydrogen are escaping through the fabric, 1 liter of air passes into the gas chamber, making a net loss of 2.8 liters. According to Graham's figures, which were determined under very different experimental conditions and with different rubber compounds, the volume loss would be $\left(\frac{3.1}{4.1}\right)$ or 76 per cent[17] of the permeability determined by the penetration method; this ratio is very close to the one found by the author. The volume-loss results given in the table were on the average 69 per cent of the values secured with the same fabrics by the penetration method. The difference between 69 per cent and the value (74 per cent) just calculated may be attributed to the fact that the hydrogen was saturated with water vapor in the volume-loss experiments and was used dry in the other method. It was shown on page 16 that the apparent permeability was 4 to 5 per cent lower when moist gas was used.

(*d*) *Absorption of Hydrogen by Rubber.*—In connection with the tests of the apparatus shown in Fig. 7 a series of determinations were made of the rate at which hydrogen is absorbed by the rubber in a balloon fabric. The tests were made by placing a fabric in the apparatus as for a determination of permeability, and then cutting slits in the fabric so as to connect both chambers of the cell. Both chambers were then filled with hydrogen, closed, and the rate

[17] Austerweil (Die angewandte Chemie in der Luftfahrt, p. 58), by erroneous reasoning, arrives at the figure 81 per cent for this relation.

at which the hydrogen was absorbed was measured in the usual way. The hydrogen absorbed was calculated in terms of liters per square meter per 24 hours. The results are shown in Table 4. A test on the cloth without the rubber coating showed no absorption of hydrogen, thus proving what was evident—that the hydrogen was absorbed by the rubber and not by the cloth.

TABLE 4.—Absorption of Hydrogen by Rubber-Coated Balloon Fabric

Fabric No.	Permeability, liters per square meter per 24 hours	Rate of absorption of hydrogen, liters per square meter per 24 hours						Milligrams of hydrogen absorbed per gram, rubber compound
		First 30 minutes	Second 30 minutes	Third 30 minutes	Fourth 30 minutes	Fifth 30 minutes	Sixth 30 minutes	
22496	15.0	4.3	.....	1.4	0.0	0.0	.....	0.08
22150	17.9	3.4	1.0	.....	.5	.0	0.0	.09
22151	15.8	1.0	1.9	.5	.0	.0	.0	.04
22152	15.8	2.4	1.0	.....	.0	.0	.....	.04
10651	11.0	.0	.....	.0	.....	.....	.....	.....
10652	20.1	.....	1.9	.....	2.4	.....	.0	.08

These experiments indicate that saturation of the rubber with hydrogen is practically complete in 60 to 90 minutes. Kayser [18] also found, using another method, that absorption was complete in about 1 hour; no further absorption was noted by him in experiments lasting 3 to 5 days. In the determinations by the volume-loss method shown in Table 2 the reading at the end of the first 30-minute period was usually about a liter higher than the average of the 8 to 10 readings taken. Although the data are not very complete, it seems evident that a higher initial reading might be partly due to this absorption of hydrogen by the rubber. It does not, however, make a significant difference in the results because of the rather large accidental errors involved in the volume-loss measurements.

(*e*) *Conclusions.*—It may be concluded from the results of these tests and many others unrecorded and from the experience of other experimenters as noted in the literature that all volume-loss methods so far developed are inferior to the penetration method both in precision and reliability. The permeability according to the volume-loss method is approximately 70 per cent of the permeability by the penetration method.

[18] Wied. Annalen der Phys. und Chem., 43, p. 547; 1891.

7. STANDARD TEST

The permeability test adopted as standard by the Bureau of Standards may be briefly described as follows: The fabric to be tested is held in a permeability cell of the size and form shown in Fig. 4, or its equivalent, and is maintained during the period of test at a temperature of 25° C. A current of pure dry hydrogen is passed over one side of the fabric under a pressure of 30 mm of water above the pressure on the other side of the fabric. Dry air, at approximately atmospheric pressure, is passed at a constant rate through the other chamber of the cell and the hydrogen passing through the fabric into the air is determined by means of a gas interferometer and meter. The hydrogen may also be determined by combustion and weighing as water. If the interferometer is used, a reading is taken every half hour until a constant permeability is indicated. If the combustion method is used, the fabric should remain in the apparatus in contact with the atmosphere of pure hydrogen for a period of one hour before beginning a test.

The permeability is calculated in liters of dry hydrogen escaping per square meter of fabric per 24 hours, the volume of hydrogen being corrected to the standard conditions of 0° C and 760 mm pressure of mercury.

8. OPERATING DIRECTIONS AND CALCULATIONS

In the preceding sections many of the details of operation such as pressure, temperature, etc., have been discussed at length. It may be well to call attention also to certain other points which must be taken account of in order to secure concordant results.

To begin with, the fabric should be firmly fastened in the cell and the area of fabric exposed to the hydrogen should be definitely known. If the faces of the cell are not exactly plane or if they are insufficiently lubricated or if the cell is not bolted together tightly, hydrogen may leak past the edge of the gas chamber and increase the area of the exposed fabric. The results will accordingly be too high and will probably be erratic.

The air current should be maintained as uniform as possible. The air can be forced through under low pressure or it may be drawn through by slightly reducing the pressure at the outlet with a water pump or other vacuum pump. To aid in maintaining a uniform pressure, a water-sealed, gas-pressure regulator may

be used. A long piece of capillary glass tubing inserted in the air line also tends to reduce fluctuations in the rate of air flow.

The hydrogen should be passed through the cell rapidly at the start of a test in order to sweep out the air as quickly as possible. When the air is removed the hydrogen need be passed only slowly in order to sweep out the air which diffuses through the fabric.

The permeability is calculated from the following equation:

$$P = \frac{S \times F \times H}{A}$$

P = permeability in liters per square meter per 24 hours.
S = rate of air passage, liters per 24 hours.
A = area of fabric in square meters.
F = factor by which indicated air rate must be multiplied to reduce the gas volume from the condition of saturation at the temperature and pressure in the meter to the volume when dry and at 0° C and 760 mm pressure.
H = percentage of hydrogen in the air stream.

The factor F is calculated as follows:

$$F = \frac{p - p_w}{760} \times \frac{273}{t + 273}$$

p = barometric pressure plus pressure above atmospheric in the meter.
t = temperature of meter.
p_w = vapor pressure of water at temperature t.

A table giving the value of F for different temperatures and pressures should be prepared if many tests are to be made.

Most of the considerations discussed in section 5 apply equally well to a method in which the hydrogen is determined by combustion with subsequent weighing as water instead of by means of an interferometer. The advantages the interferometer offers in point of speed and precision have already been pointed out. If a suitable interferometer is not available, however, the hydrogen may be determined by combustion; in fact, this is the customary method in commercial use.

To secure correct results by combustion, it is necessary that the air and hydrogen from the cell be perfectly dried; that the hydrogen be completely burned; that the water formed be completely absorbed and its weight correctly determined. This can be done with sufficient accuracy if the proper precautions are taken.

The efficiency of drying with any apparatus and drying agent should be tested by blank runs. It is desirable to use two absorption tubes in series in order to determine the efficiency of drying in the first tube. When the second drying tube begins to absorb increasing amounts of moisture, the first tube should be refilled.

The combustion of the hydrogen may be accomplished in a number of ways, such as by passing over heated copper oxide, platinized asbestos, platinized quartz, palladium black, glowing platinum wires, etc. Complete combustion can be secured by any of these catalysts if the proper temperature is employed and the gas is not passed through the combustion tube too rapidly. In any case it is well to determine by experiment that the combustion is complete under the conditions of use. It is important that the rate of passage of the air be not too rapid to prevent efficient drying and complete combustion.

Since the amount of water collected is usually small, every precaution should be taken in weighing the glass absorption tubes. It is desirable that a counterpoise of as nearly the same size and shape as the absorption tube be used in weighing. The absorption tubes should be wiped with a damp cloth and hung in the balance case or a suitable container to permit them to assume the temperature of the balance before weighing. Rubbing the glass while dry is likely to produce electrostatic charges on the glass which prevent accurate weighing.

9. ACCURACY OF METHODS

The accuracy with which the permeability of a fabric can be determined depends upon the accuracy with which the various factors of the test, such as concentration of hydrogen, etc., can be determined, and is closely associated with the question of uniformity of fabric. Some fabrics show very close agreement on duplicate tests and give evidence of being very uniform. Fabric No. 24579 is a good example of this. Tests on eight different test pieces of this fabric showed permeabilities between 8.6 and 8.9 liters. Experience with this fabric indicates that a great many of the differences noted between duplicate tests on other fabrics are caused by real variations in the permeability of the fabric and not by unobserved errors of testing. If the fabric contains "pinholes," the variations in permeability of test pieces may be very large because it is unlikely that the small holes will be uniformly distributed and be uniform in size. One sample which showed

"pinholes" gave tests ranging from 14.5 to 43.5 liters. In general, duplicate tests on good fabrics show an agreement within approximately 1 liter in the range of 10 to 20 liters.

With the standard cell having an area of 250 cm^2 an interferometer giving the concentration of hydrogen to 0.01 per cent and a 1/20 cubic foot meter graduated in thousandths of a cubic foot and read to ten thousandths of a cubic foot, it is possible to keep the probable experimental errors below 5 per cent. Under routine testing conditions the accuracy may vary from 5 to 10 per cent. Greater variations than this in the uniformity of the fabric are commonly met with. The precision attained—that is, the agreement between successive tests on the same test piece—is somewhat greater than the absolute accuracy attained.

If the combustion method is used, about the same accuracy can be secured if the proper precautions to secure complete drying, combustion, and absorption are taken. Because of the length of time necessary for a test, check tests are not usually run, and furthermore it is necessary to obtain the average permeability over a period of several hours unless a very large cell is used.

10. SUMMARY

The various methods for determining the permeability of balloon fabrics to hydrogen are described in this paper; the precise and rapid method used at the Bureau of Standards is described in detail. The phenomenon of the passage of gases through rubber by solution in the rubber is discussed in relation to testing methods. Data are given to show the effect upon the apparent permeability of different experimental conditions such as temperature, pressure, humidity of the gas, duration of test, etc. A knowledge of the effect of these factors enables one to compare results of tests made under different conditions. It has been shown that methods which depend upon the loss of volume of hydrogen confined by a sample of the fabric give results which are about 70 per cent of those obtained by the standard method which measures the volume of hydrogen penetrating the fabric. This is due to the mutual permeability of the fabric to air and hydrogen.

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